

METAL IONS REMOVAL FROM WASTEWATER BY ADSORPTION

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ABSTRACT

Three different carbonaceous adsorbents consisting of (i) commercially available lignin (L); (ii) carbon soot produced by arc evaporation of graphite rods (AC); and (iii) commercially available carbon (RC) were employed for the removal of hexavalent and trivalent chromium, and the cations of lead and zinc. AC carbon was found to selectively adsorb only the hexavalent form of chromium which exists as a number of anionic species in the water. Insignificant metal cation adsorption was observed with AC. However, lignin is found to adsorb all the metal ions employed in the study. RC used in this investigation adsorbs only the metal cations and does not remove the hexavalent form of chromium used. Equilibrium as well as kinetic data obtained are analyzed in light of a mathematical model developed which assumes that the overall metal removal rate is controlled by the rate of mass transport of solute from bulk to the surface of the adsorbent.

INTRODUCTION

The presence of heavy metals in the environment is a major concern due to their toxicity to many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end products. Thus, treatment of aqueous wastes containing soluble heavy metals requires concentrations of the metals into smaller volume followed by recovery or secure disposal. Heavy metals can be found in a variety of industries, in particular mining, metal processing, finishing and plating. Effluents from these industries contain heavy metals, the concentrations of which are regulated by governmental agencies. Thus, it is often required to remove heavy metals before discharge of various effluents. The major techniques employed for heavy metal removal from industrial wastewaters include precipitation, reduction, ion-exchange, and adsorption. Attempts have been made by several researchers to develop alternate inexpensive methods for heavy metal removal using industrial waste materials (discarded tires, fly ash, sludge), agricultural products, and byproducts (starch, tree barks, onion skin, coconut shell, palm pressed fibers, lignin), and naturally occurring minerals (coal, peat moss, pyrite).

The choice of adsorbents used in this study was motivated by the following rationale. Lignin, an inexpensive naturally occurring material is a component of woody biomass. It is available in large quantities as a byproduct from the paper and pulp industry. Lignin contains many oxygen functionalities such as phenols and ketones which can serve as adsorption sites for binding heavy metals. Carbon produced from graphite rods by electrical arcing method under inert atmosphere is expected to have unusual properties. The carbon soot produced under these conditions also leads to fullerene formation. A commercially available activated carbon (RC) was used as a control to compare the metal removal properties of lignin (L) and the carbon produced by arc evaporation of graphite rods (AC).

EXPERIMENTAL METHODS

Lignin was obtained from Westvaco Corporation. It is characterized as Indulin AT, a purified powder form of kraft lignin, which is completely free of all hemicellulosic materials. The arc-assisted synthesis of carbons (AC) is reported in a previous paper(1). The method involves arcing of graphite electrodes under flowing helium atmosphere. The alternating current applied to the electrodes ranged from 100-160 amperes. The application of this high current resulted in vaporization of the graphite. The condensed soot was collected and used as an adsorbent. In addition, a commercially available activated carbon (RC), Darco TRS obtained from American Norit Company was also used as an adsorbent for the metal ion removal from aqueous solutions.

Batch sorption experiments were conducted at a constant room temperature of 25 °C using a 500 ml Erlenmeyer flask. The stirred reaction mixture consisted of a total volume of 250 ml. When necessary, the initial pH of the solution was adjusted. The metal concentration was determined by inductively-coupled plasma spectroscopy (ICP).

RESULTS AND DISCUSSION

The effect of initial chromium concentration on the removal of hexavalent chromium at solution pH (initial) of 4.5 using the arc assisted produced carbon (AC) is shown in Figure 1. The adsorbent loading used was 5 g/l and the experiments were conducted for a period of 24 h. The chromium removal (%) is found to increase with the initial metal concentration reaching a maximum value of approximately 94%, however, with a further increase in metal concentration, the removal is found to decrease. Similar albeit lower hexavalent chromium removal vs. concentration trends are observed when lignin is used as an adsorbent in the metal ion containing solution prepared at an initial pH value of 2.5 (Figure 1). Up to 53% metal removal was observed in the case of lignin. It must be noted that when the commercially available activated carbon (RC) was used very small amount of hexavalent chromium removal was obtained. For example, the use of initial metal concentration of 20 ppm in experiments conducted at three different initial pH values of 2.5, 3.0 and 4.5 resulted in 24.6, 14.0, and 9.1% chromium removal, respectively. The data reported in Figure 1 were used to prepare adsorption isotherms. AC adsorbent does not seem to follow either Langmuir or Freundlich isotherm models. The maximum adsorption capacity for the Cr^{6+} /AC system was found to be 8.9 mg/g of sorbent. On the contrary, data for the Cr^{6+} /lignin system represents a relatively good fit to the Langmuir equation and can be expressed by the following equation:

$A^{-1} = 2.9 \cdot C_e^{-1} + 0.18$, where A is the adsorption capacity and C_e is the equilibrium concentration in mg/l. The maximum adsorption capacity is estimated to be 5.64 mg/g of sorbent.

The data on removal of trivalent chromium at an initial pH value of 3.0 as function of the metal concentration for the three adsorbents are shown in Figure 2. Experiments were conducted for 24 h using 5 g/l of adsorbent loading. RC adsorbent is found to remove practically all the metal present in the solution. In the case of lignin, about 90% metal removal is observed at low metal ion concentrations. However, an increase in metal concentration results in corresponding lower removal (%). On the other hand, essentially no trivalent chromium removal is noted when the arc-assisted produced carbon (AC) was used in these experiments.

In the experiments involving metal cations of lead and zinc, practically no metal removal was observed when the arc-assisted produced carbon (AC) was used especially at low pH values. For example, in the case of experiments involving lead (Pb^{2+}), 0, 2 and 25% metal removal was noted at pH values of 3.0, 4.5 and 9.0 respectively. RC carbon was observed to remove 100% lead at pH values ranging from 2 to 9.5. Lignin also showed a great affinity for lead. The metal removal (%) increases with pH. For example, the removal of lead by lignin is 47, 74 and 98% at pH values of 2.0, 2.5 and 3.0 respectively. Both, RC and lignin showed 100% zinc removal while no metal removal was observed for AC up to a pH value of 6.0. AC showed about 30% zinc removal at a pH value of 9.0.

The data obtained above can be explained as below. Hexavalent chromium is present in aqueous solutions mainly as anionic chromate species. Therefore, AC carbon is capable of removing this form of chromium as it is hypothesized to contain positive charge on the surface. It must be noted that this carbon is produced by arc evaporation of graphite rods in the absence of air or oxygen. This hypothesis also explains the inability of this form of carbon to remove cations of chromium, lead and zinc at relatively low pH values. At high pH values the surface charges of AC are neutralized, therefore it is able to adsorb limited amount of metal cations. Lignin contains mainly oxygen functionalities, therefore it is able to remove metal cations in addition to the anionic chromate species. On the other hand, RC is activated using steam or air, therefore its surface has mainly oxygen functionalities which serve as negatively charged sites for binding only the metal cations.

REFERENCES

1. Weston, A. and Murthy, M., "Synthesis of Fullerenes: An Effort to Optimize Process Parameters," Carbon, 34, 10, 1267-1274, 1996.

Figure 1. Hexavalent Chromium Removal vs. Concentration

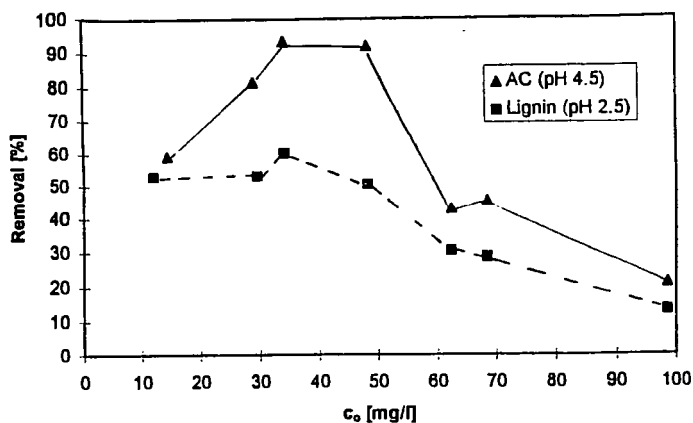


Figure 2. Trivalent Chromium Removal vs. Concentration

